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Modeling of excitonic properties in tubular molecular aggregates

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Summary

Organic molecules characterized by strong interaction with light are called pigments. When closely packed in assemblies, known as *molecular aggregates*, pigments work together to efficiently absorb light and redistribute its energy. This principle of efficient collective work was carefully designed by Nature and is implemented as a part of the photosynthesis—the process used by plants, algae, and photosynthetic bacteria to convert solar energy into chemical energy to sustain life on Earth. A crucial role in photosynthesis is indeed played by molecular aggregates of photosynthetic pigments—called light-harvesting antennae—that are responsible for capturing light and transferring its energy to a reaction center, where the conversion of light into chemical energy takes place. Molecular aggregates can also be produced artificially via self-assembly. Depending on the intermolecular forces guiding the self-assembly process, molecular aggregates can be obtained in a variety of shapes at the nanoscale, such as linear chains, rings, films or tubes, which make them attractive for the development of functional nanoscale materials.

The intriguing optical properties of molecular aggregates originate from their collective behavior. The collective optical response of the molecular aggregate is fundamentally different from the sum of the responses of the individual molecules. Upon interaction with light, due to the energy of the absorbed photon, a molecule is promoted from its ground state to an excited state. In the case of a molecular aggregate, the excited state is collectively shared by the molecules of the aggregate. Such collective excited states are called *Frenkel excitons*. The excitons dictate the optical and energy transport properties of the molecular aggregate. Due to the symmetry of the system, for example, linear or circular, some excitons are special—they collect most of the oscillator strength giving rise to an enhanced optical response as compared to individual molecules. As a result, other states are dark, meaning they are not visible in the optical spectrum.

In perfectly ordered aggregates, collective excited states are shared, or delocalized, over all molecules. In reality, however, aggregates are embedded in a medium—for example, a solvent or a protein scaffold—where each molecule feels a slightly different environment. The presence of such disorder in the system affects the delocalized nature of the excitons, for example, by confining them over a smaller space. As a consequence, optical and energy transport properties are also affected.

Understanding of the relationships between structure and excitonic properties is an exciting research area that attracts the attention of a lot of scientists. Besides

gaining fundamental knowledge about Nature, there is also technological interest arising from the demand for new and more efficient functional materials for optical and electronic applications. However, the current lack of information about the details of the molecular packing in molecular aggregates and the presence of the disorder makes it a challenging task to study real systems. Structural details can be elucidated by theoretical modeling of the optical spectra.

The work described in this thesis is focused on the theoretical modeling of the excitonic properties in tubular molecular aggregates. As a particular model system, tubular aggregates composed of cyanine dyes are studied. This system is especially interesting as it resembles the light-harvesting antennae of green sulfur bacteria—the most efficient photosynthetic system known. Like natural light-harvesting antennae, these synthetic nanotubes are formed by thousands of closely packed molecules organized in a tubular geometry. The remarkably uniform structure of these synthetic nanotubes provides an excellent model system for studying how molecular organization tailors the excitonic properties.

Chapter 2 unravels the optical signatures of tubular molecular aggregates using theoretical modeling of the optical spectra. Experimentally, it is shown that a slight chemical alteration of the original dye molecule results in the increase of the radius of the tubular aggregate. This increase of the radius is accompanied by spectral changes. Understanding the origin of the observed changes in the optical spectra forms the main motivation of Chapter 2. In order to elucidate whether the observed optical changes originate from the increased radius or from changes in the molecular packing within the aggregate, a phenomenological structure—that is, a structure with a simplified molecular representation—is used to calculate the optical spectra. The findings of this chapter reveal that the observed spectral changes originate purely from the radial growth, which affects the collective optical properties of the tubular aggregates. Moreover, the findings open the way to study size effects under well-controlled conditions.

The findings of Chapter 2 demonstrated that the physical size affects the excitons, in turn resulting in changes of optical properties. This inspired Chapter 3, where the problem of size effects on exciton delocalization is investigated in a systematic way. Here, the study of how the system's size—radius and length—affects exciton delocalization in the presence of disorder is described. This chapter shows the limits where the length and the radius confine the excitons, and where the disorder is the constraining factor.

Despite the utility of using phenomenological models to calculate optical spectra of molecular aggregates, these models are not accurate enough to explain some of the observed spectral signatures. Besides, they are limited in predictive power, which is crucial for obtaining design rules to develop new functional materials. The need to improve modeling techniques for these types of system forms the basis of Chapter 4.

Here, it is shown that accurate insights can be obtained using a multiscale approach that combines classical (molecular dynamics) and quantum mechanical (exciton modeling) techniques. The obtained model provides microscopic details of the structure, its interaction with the environment, and the effect of the molecular packing and the disorder from the environment on the optical properties. Such a detailed model can further be used to accurately study energy transfer in these systems.

Theoretical methods to study energy transfer in large molecular aggregates, such as the ones studied in this thesis, should provide accurate results and be computationally feasible in order to be useful. Despite a number of available methods, such methods are still not well-established. This motivated the work presented in Chapter 5, which studies the validity, performance, and efficiency of several popular theoretical methods. A simple model system, the energy transfer from a donor molecule to an acceptor ring aggregate of varying size, is used to compare the multichromophoric Förster resonance energy transfer (MC-FRET) method, the numerical integration of the Schrödinger equation (NISE) method, and the Haken-Strobl-Reineker (HSR) model, each of these methods having different approximations. These methods are validated against the numerically exact Hierarchy of Equations of Motion (HEOM) method. A large parameter space of the system and the environment is considered in the study. The most reasonable results are obtained for the NISE method, which is predicted to perform well to study energy transfer in large molecular systems.

To conclude, the work described in this thesis contributes to the fundamental knowledge of the scientific community about molecular aggregates with interesting excitonic properties. The obtained results can be used in further studies towards the design of materials with fine-tuned optical behavior for optoelectronic applications, such as artificial photosynthetic systems or energy transport nanowires.

Samenvatting

Organische moleculen die gekarakteriseerd worden door een sterke interactie met licht worden pigmenten genoemd. Veel van dat soort moleculen vormen spontaan grote assemblages, ook bekend als moleculaire aggregaten. In dergelijke assemblages werken de pigmenten samen om efficiënt licht te absorberen en de energie daarvan snel te verspreiden. Dit principe van efficiëntie door collectiviteit is nauwkeurig ontworpen door de natuur en is geïmplementeerd als onderdeel van de fotosynthese. Dat is het proces dat gebruikt wordt door planten, algen en sommige bacteriën om zonne-energie om te zetten in chemische energie (brandstoffen) en om zo leven op aarde te laten bestaan. Een cruciale rol in het fotosynthetische proces is weggelegd voor moleculaire aggregaten van pigmenten, zogenaamde light-oogstende antennes. Deze antennes zijn verantwoordelijk voor het absorberen van zonlicht en het transporteren van de daarmee ingevangen energie naar reactiecentra, waar de conversie naar chemische energie plaatsvindt. Moleculaire aggregaten kunnen ook in een laboratorium geproduceerd worden via synthetische zelf-assemblage. Afhankelijk van de intermoleculaire krachten die een rol spelen bij de zelf-assemblage, kan een variatie aan moleculaire aggregaten ontstaan op de nanometerschaal zoals lineaire ketens, ringen, monolagen, of buisjes, wat ze interessant maakt voor de ontwikkeling van functionele nanomaterialen.

De fascinerende optische eigenschappen van moleculaire aggregaten komen voort uit collectief gedrag. De collectieve reactie van moleculaire aggregaten op licht is fundamenteel anders dan de som van de reacties van de individuele moleculen. De interactie met licht zorgt ervoor dat een molecuul gepromoveerd wordt van zijn toestand met de laagste energie (grondtoestand) naar een met een hogere energie (geëxciteerde toestand). In het geval van een moleculair aggregaat worden de geëxciteerde toestanden gedeeld door vele moleculen in het aggregaat. Een dergelijke collectieve geëxciteerde toestand wordt een Frenkel exciton genoemd. Deze excitonen bepalen de optische en energietransport eigenschappen van het moleculaire aggregaat. In systemen met een sterke mate van symmetrie, zoals een periodiek lineair of ringvormig aggregaat, zijn sommige excitonen speciaal, in de zin dat zij een aanzienlijk deel van alle interactiesterkte van de moleculen met licht in het aggregaat verzamelen. Deze zogenaamde superstralende toestanden reageren daardoor veel sterker op licht dan individuele moleculen. De andere toestanden zijn donker, wat betekent dat deze geen interactie hebben met licht en dus ook niet zichtbaar zijn in het optische spectrum.

In perfect geordende aggregaten zijn collectief geëxciteerde toestanden gedeeld, of

gedelokaliseerd, over alle moleculen. In de praktijk zijn de aggregaten echter meestal onderdeel van een medium, bijvoorbeeld een oplossing of een eiwitcomplex, waarin de omgeving van elk molecuul een klein beetje verschillend is. De aanwezigheid van dergelijke wanorde in het systeem heeft invloed op het gedelokaliseerde karakter van de excitonen, met name zorgt die voor het beperken van het aantal moleculen waarover het exciton zich verspreidt. Als gevolg worden ook de optische en energietransport eigenschappen beïnvloed.

Het begrijpen van de relatie tussen structuur van de aggregaten en de eigenschappen van de excitonen is een belangrijk onderzoeksgebied, waarin veel onderzoekers werken. Naast het vergaren van fundamentele kennis over de natuur, is er ook technologische interesse die zich bijvoorbeeld richt op de vraag naar nieuwe en efficiëntere materialen voor optische en elektronische toepassingen. Het gebrek aan informatie over de details van de moleculaire structuur van veel moleculaire aggregaten en de aanwezigheid van wanorde maken het een uitdagend probleem om realistische systemen te beschrijven en hun optische eigenschappen te verklaren en te voorspellen. Het theoretisch modelleren van optische spectra op basis van aangenomen of berekende structuren kan daarbij zeer behulpzaam zijn.

Het werk beschreven in dit proefschrift richt zich op het theoretisch modelleren van de eigenschappen van excitonen in buisvormige moleculaire aggregaten. In het bijzonder worden buisvormige aggregaten bestaande uit cyanine pigmenten bestudeerd. Dit systeem is bijzonder interessant omdat het de licht-oogstende antennes van groene-sulfaat bacteriën nabootst. Deze antennes zijn onderdeel van het meest efficiënte fotosynthetische systeem tot op heden bekend. Zoals natuurlijke antennes, worden ook de synthetische nano-buisjes die in dit werk bestudeerd worden gevormd door duizenden dicht samengepakte moleculen die georganiseerd zijn in een buisvormige geometrie. De bijzonder uniforme structuur van deze synthetische nano-buisjes maakt ze ideale modelsystemen voor de studie naar hoe moleculaire structuur de excitonische eigenschappen beïnvloedt.

Hoofdstuk 2 legt de optische signatuur bloot van buisvormige moleculaire aggregaten door middel van het theoretisch modeleren van de optische spectra en vergelijking met metingen. Experimenteel is aangetoond dat een kleine chemische aanpassing van het originele pigment resulteert in een toename van de straal van het buisvormige aggregaat. Deze toename van de straal gaat samen met een verandering van het optische spectrum. Het begrijpen van deze verandering vormt de belangrijkste motivatie voor hoofdstuk 2. Hiertoe, wordt een fenomenologische structuur (een aangenomen plausibele structuur) gebruikt om de optische spectra te berekenen. De resultaten onthullen dat de waargenomen spectrale verandering alleen veroorzaakt wordt door de toename in de straal en niet door een verandering in de manier waarop de moleculen in de buisjes zijn samengepakt. De resultaten van dit hoofdstuk openen ook de deur voor verdere studies naar het effect van de straal van het aggregaat op

andere optische eigenschappen onder goed gecontroleerde omstandigheden.

De resultaten van hoofdstuk 2 laten zien dat de afmetingen van een aggregaat invloed hebben op de eigenschappen van de excitonen, hetgeen vervolgens veranderingen teweegbrengt in de optische eigenschappen. Dit vormt de inspiratie voor hoofdstuk 3, waar op systematische wijze de effecten van de afmetingen van aggregaten op excitondelokalisatie worden onderzocht. In het bijzonder wordt bestudeerd hoe straal en lengte van een buisvormig aggregaat de excitondelokalisatie beïnvloedt in de aanwezigheid van wanorde. De resultaten laten zien dat, in tegenstelling tot wat gewoonlijk wordt aangenomen, onder experimentele omstandigheden niet altijd de wanorde, maar ook de afmetingen beperkend kunnen zijn voor de excitondelokalisatie.

Ondanks het grote nut van fenomenologische modellen om optische spectra van moleculaire aggregaten te berekenen en te begrijpen, zijn dergelijke modellen niet accuraat genoeg om alle experimentele waarnemingen te verklaren en om nieuwe aggregaten met specifieke eigenschappen te ontwerpen en zo nieuwe materialen te ontwikkelen. De noodzaak om de modelleringstechnieken voor dit type systemen te verbeteren vormt de basis van hoofdstuk 4. In dit hoofdstuk wordt aangetoond dat ook voor zeer grote buisvormige aggregaten nauwkeurig inzicht verkregen kan worden door middel van een gelaagde aanpak die een combinatie is van klassieke (moleculaire dynamica) en kwantummechanische (exciton modellering) technieken. Het zo verkregen model omvat microscopische details van de structuur, haar interactie met de omgeving en het effect van moleculaire stapeling en de wanorde van de omgeving op de optische eigenschappen. Dergelijke gedetailleerde modellen kunnen ook gebruikt worden om het energietransport in deze systemen nauwkeurig te bestuderen.

Theoretische modellen om energietransport te bestuderen in grote moleculaire aggregaten, zoals bestudeerd in dit proefschrift, dienen nauwkeurige resultaten te genereren en bovendien computer-technisch haalbaar te zijn voordat ze nuttige resultaten kunnen produceren. Hiertoe zijn in het verleden een aantal methodes ontwikkeld, alle met hun voordelen en nadelen. Dit vormde de motivatie voor het werk dat gepresenteerd is in hoofdstuk 5, waarin toepasbaarheid, prestatie en efficiëntie van verschillende populaire theoretische methoden om energietransport te beschrijven worden bestudeerd. Hiertoe wordt dit transport bestudeerd in een eenvoudig modelsysteem, bestaande uit een donormolecuul waarvandaan energie kan worden overgedragen naar een ringvormig aggregaat van acceptormoleculen. Voor dit systeem wordt een drietal benaderende methodes (de zgn. "MultiChromophoric Förster Resonant Energy Transport" (MC-FRET) methode, de "Numerical Integration of the Schrödinger Equation" (NISE) methode, en het Haken-Strobl-Reineker (HSR) model) vergeleken met de numeriek exacte "Hierarchy of Equations of Motion" (HEOM) methode. Een groot deel van de parameterruimte van het systeem en de omgeving is meegenomen in deze studie. De resultaten laten zien dat van de benaderende methodes de NISE-methode in het algemeen het beste voldoet en gebruikt

kan worden voor het beschrijven van energietransport in grote systemen, bestaande uit veel moleculen.

Samenvattend, het werk beschreven in dit proefschrift draagt bij aan de fundamentele kennis over moleculaire aggregaten met interessante excitonische eigenschappen. De behaalde resultaten kunnen gebruikt worden voor vervolgstudies naar het ontwerp van materialen met bepaalde gewenste eigenschappen voor optoelektronische applicaties, zoals kunstmatige fotosynthetische systemen of nano-draden voor energietransport.

List of publications

- A. S. Bondarenko, T. L. C. Jansen *Application of two-dimensional infrared spectroscopy to benchmark models for the amide I band of proteins*, *J. Chem. Phys.* **2015**, *142*, 21.
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- A.S. Bondarenko, T.L.C. Jansen, and J. Knoester *Exciton localization in tubular molecular aggregates: size effects and optical response*, **2019**, in preparation.

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Anna